

TRANSPORT PROPERTIES OF PVA BASED ION CONDUCTING POLYMER ELECTROLYTE COMPLEXED WITH SODIUM ACETATETRIHYDRATE

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ABSTRACT

In the present work, an attempt has been made to prepare solid polymer electrolyte systems (Poly Vinyl Alcohol and sodium acetatetrihydrate) by solution-cast technique. The optical spectrum revealed that the absorption peaks in ultraviolet region (360-375nm) and is attributed to polymer chain complexed with salt. Moreover, the D.C. Conductivity as well as transport properties (temperature range 303K to 373K) were carried out. The conductivity results reveal conduction mechanism is of Arrhenius-type thermally activated process. The highest conductivity is found to be 5.57×10^{-6} S/cm at 373 K, for sample 60:40 of sodium acetatetrihydrate in PVA. Whereas in transport properties, the transport number of the mobile species in the polymer electrolytes was calculated by HebbWagner's polarization technique. The total charge transport of ionic was found at 0.98 in this polymer electrolyte system. These results indicate that the charge transport in the polymer electrolytes is mainly due to Na^+ ions.

KEYWORDS: Solid Polymer Electrolyte, Ionic Conductivity, Solution Casting Technique, Transport Properties, UV- Absorption Peak

INTRODUCTION

Now-a-days polymer electrolytes are mainly focused because of their mechanical, chemical, and thermal properties (1). Polymer electrolytes have received attention towards it because of their potential applications in solid state batteries, chemical sensors and electro chemical devices (Gray1997 Sanchez *etal*1998 Wang *etal*2002). These polymer electrolytes have the high ionic conductivity, good mechanical properties and excellent electro chemical stability (2, 3). Though there are many polymers available, poly vinyl alcohol (PVA) is considered among them. PVA is a polymer with carbon chain back bone attached with hydroxyl groups and non toxic. It is biocompatible, biodegradable simple to prepare, has excellent mechanical strength and is chemically and thermally stable (4,5). PVA is a partial crystalline with glass transition temperature T_g of 363 K(5), and has host in electrolyte systems.

PVA doped with sodium salts was first reported by P. V. Wright and are more popularly known as solid polymer electrolytes (SPEs) (6). M. B. Armand realized application based on PVA electrolytes to lithium batteries and are now one of the major applications (7). These reports led to tremendous research and development has been carried out on polymer electrolytes for ambient temperature rechargeable lithium and solid ion batteries. In the past few years, SPEs have gained considerable attention because of their potential in high-energy density batteries, sensors and fuel cells. The ionic conductivity and the cation transport number represents the performance and stability in Solid polymer electrolyte systems, which allows high performance operation with a high specific energy density (8,9). In this paper, the authors discusses on solid ion conducting polymer electrolyte based on (PVA+ $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) system. Synthesis method, optical and electrical properties, such as UV-Visible spectroscopy, composition dependent conductivity, d.c Conductivity range at

308-373 K and transport number measurements were performed to characterize these polymer electrolytes. The results are reported in this present paper.

EXPERIMENTAL

In this method PVA of very high purity (99 %, Aldrich) and having a conductivity of $\approx 9 \times 10^{-9}$ S/cm is mixed with a fine powder of sodium acetate trihydrate salt ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$; 99 %, Aldrich). The films were prepared in the stoichiometric ratios (80:20), (70:30), and (60:40) by an “isothermal immersion” technique using double distilled water as solvent. The chemicals were used directly without any further purification. The optical absorption studies were performed on Jasco-V-670, in the range of 200-1100 nm at room temperature. D. C. conductivity and transport properties were carried out on homemade conductivity setup. Temperature can be varied in the range 303-373 K (using thermostat). Both current (mA) versus temperature (K) as well as current (mA) versus time (s) were recorded using Keithley electrometer (Keithley Inc., model 6514). For transport properties a d c bias (step potential 2.5V) is applied.

RESULTS AND DISCUSSIONS

UV - Visible Studies

To investigate the formation and their temperature dependence in sodium acetate, UV-vis spectroscopy was used as optical characterization method. This is due to the fact that their clusters exhibit a characteristic UV- vis absorption band in the ultra violet region (UV-vis region). Figure shows the UV absorption spectra of pure PVA + sodium acetate trihydrate (60:40) solid electrolytes at ambient temperatures 373K, that pure PVA has it also observes that no absorption peak in the region 400 to 500nm. while a wide absorption peak observed at 426nm for PVA+ sodium acetate trihydrate (60:40) solid electrolytes which can be attributed to the surface plasmon bond. And it represents that the absorption peak occurs at maximum 420 to 520 nm is related to the information figure shows UV-vis absorption spectra for sodium acetate trihydrate solid electrolyte at various temperatures. It observes that the maximum of the peak increases from 0.61 at 303K to 1.2 at 393K with an increasing temperatures which states an increase percentage of sodium acetate, it has been reported that polymers which contain hydroxyl, carboxyl and amide groups are responsible for Na^+ ion reduction

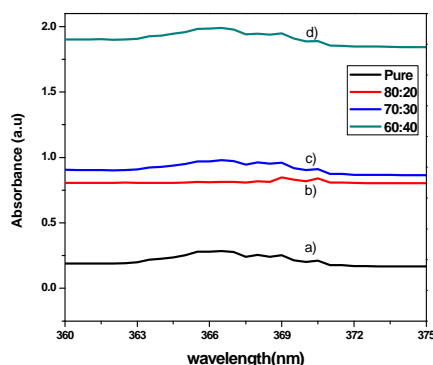


Figure 1: UV- Vis Absorption Spectrum of a) Pure b) PVA + $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (80:20) c) PVA+ $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (70:30) d) PVA+ $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (60:40)

The difference in logarithmic conductivity sigma as a function for different concentrations of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in PVA with various temperature's which shown in figure 2 .The resulting data observed that the conductivity of pure PVA is 10^{-9}Scm^{-1} at R_T , which changes at 10^{-6}Scm^{-1} with 10% wt $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$.The conductivity which is increasing by adding

the salt to the polymer. The comparison of conductivity of PVA+CH₃COONa3H₂O electrolyte reveals that the conductivity is increased by a factor of 10% because of by adding the salt concentration. From the above figure 2 it reveals that their increase in conductivity by adding the salt concentration.

The conductivity of pure PVA is about 10⁻⁹Scm⁻¹ at R_T and the conductivity value increases with increase of salt concentration of CH₃COONa3H₂O and change in its magnitude is order of 10³ times in PVA+CH₃COONa3H₂O (80:20,70:30and60:40) polymer electrolyte membranes which evaluated to that of pure PVA polymer .

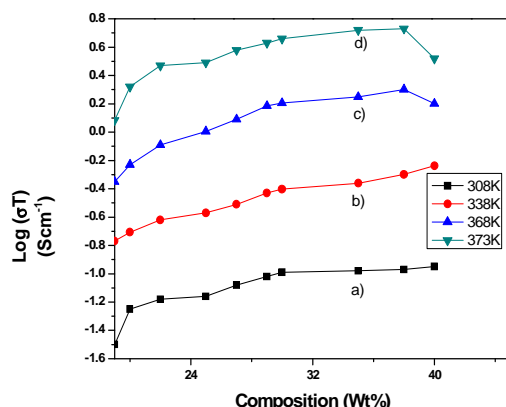


Figure 2: Weight Composition Studies of a) 308K b)338K c) 368K d) 373K

DC Conductivity Result Analysis

The difference in logarithmic conductivity functions of CH₃COONa3H₂O concentration in PVA.Sodium acetate trihydrate at various temperatures is shown and the values are given in table 1. The conductivity of pure PVA is found as 9.73x10⁻⁹Scm⁻¹ at room temperature, the conductivity increases with increase in charge carriers by adding the CH₃COONa3H₂O which result that the conductivity is high at 5.57x10⁻⁶S/cm for 40wt% at 373K. The function of temperatures for different ratios of CH₃COONa3H₂O of ionic conductivity in solid polymer electrolyte is as shown in figure 3.

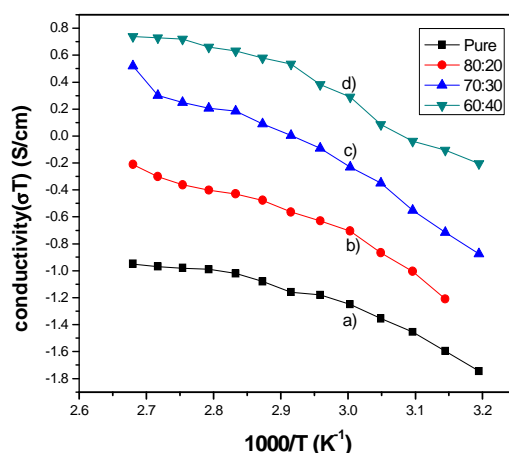


Figure 3: DC Conductivity Analysis a) Pure b) PVA+CH₃COONa3H₂O (80:20)
c) PVA+CH₃COONa3H₂O (70:30) d) PVA+CH₃COONa3H₂O (60:40)

In the above plot shows that the conductivity increases as with temperature because of hopping mechanism between structure relaxations, coordinating sides and segmental motion of the polymer .And also shows Arrhenius behavior for the two regions (I&II). Where it is observed that in region I, the conductivity raises slowly while in region II the rate of conductivity is very high .This is because at melting point the semi crystals changes to amorphous region. After the amorphous region slightly increases in region II as a result of which polymer chain obtained faster internal modes for which bond rotation produce segmental motion .which relates hopping of ions with in between the polymer chains such that the conductivity becomes high. Same results are obtained for reported for polymer electrolytes based on PVA. The conductivity studies can be calculated by $\sigma_{dc} = L/RA$.

For measuring the D.C conductivity the SPE films are cut in to small area of 2 cm diameter and placed in between two identical circular smooth and cleaned silver plates electrodes under spring pressure to ensure good electrical contacts between the electrodes and the sample, this enables us to avoid the parasite capacitance induced in presence of air interstices at the inter faces between the sample and the electrode.

A plot of sigma DC verses $1000/T$ for pure PVA in the temperature range 30-100°C is as shown in figure 3, the conductivity is found to be at 5.57×10^{-6} S/cm. The conductivity increases with temperature which indicates complete amorphous phase. The hopping mechanism in polymer films can be well explained to measure the conductivity.

Figure 4 illustrates the variation of activation energy with $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ concentration. It is also explains that (PVA+ $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) (60:40) represents the lowest activation energy and highest conductivity.

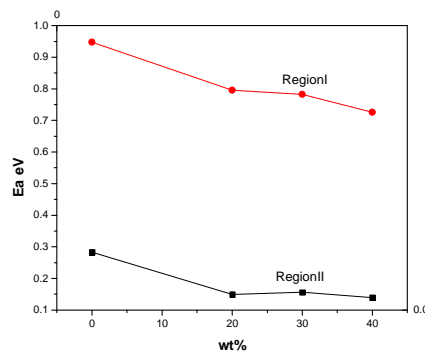


Figure 4: Activation Energy with $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ Weight Percentage

Table 1: Conductivity, Activation Energies and Transport Numbers of (PVA+ $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) Polymer Electrolyte System

Films	Conductivity at RT (Scm^{-1})	Conductivity at 373 K (Scm^{-1})	Activation Energies (EV)		Transference Numbers	
			Region I	Region II	Tion	Tele
Pure PVA	9.73×10^{-9}	8.71×10^{-8}	0.948	0.2831	-	-
PVA+ CH_3COONa (80:20)	1.26×10^{-8}	1.32×10^{-7}	0.7857	0.1492	0.96	0.04
PVA+ CH_3COONa (70:30)	4.42×10^{-7}	2.41×10^{-6}	0.7927	0.1563	0.97	0.03
PVA+ CH_3COONa (60:40)	3.28×10^{-7}	5.57×10^{-6}	0.1257	0.1394	0.98	0.01

Transport Number Studies Analysis

The total ionic and total electronic transport number plays a major role in study of conductivity in polymer electrolyte systems. The transport number relates to t_{ion} and t_{ele} in polymer film of PVA+CH₃COONa3H₂O can be calculated by using Hebb Wagner's polarizing method. In this method DC current was screened as the operating time on application of DC voltage across the sodium (anode)/polymer electrolyte/Carbon powder, electrolyte film powder (cathode).when 2.5volts is applied across to the electrolyte cell, the time plots vs current can be measured and it is shown in figure 5.

Table 2: Values of Mobility and Transport Number for Pure PVA and PVA+CH₃COONa3H₂O Electrolyte Systems

Electrolytes	Transference Number (t_{ion})	Mobility (μ) (in m^2/Vs)
Pure PVA	-	$0.94 \times 10^{-8} m^2/Vs$
PVA+CH ₃ COONa (80:20)	0.96	$1.12 \times 10^{-8} m^2/Vs$
PVA+CH ₃ COONa (70:30)	0.97	$2.07 \times 10^{-8} m^2/Vs$
PVA+CH ₃ COONa (60:40)	0.98	$2.37 \times 10^{-8} m^2/Vs$

Since the transport number of t_{ele} values are negligible, from that it is observed that the mobility of electrons in solid polymer film is very low.

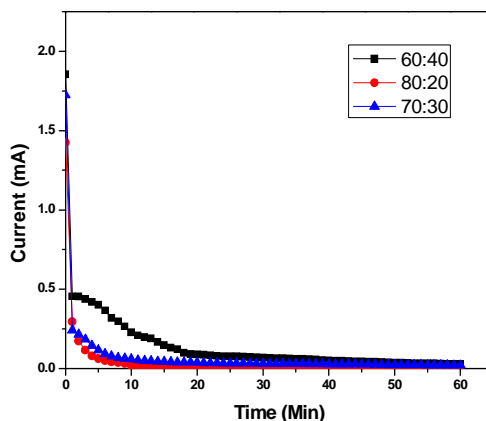


Figure 5: Transport Characteristics a) PVA+CH₃COONa3H₂O (60:40) b) PVA+CH₃COONa3H₂O (80:20) c) PVA+CH₃COONa3H₂O (70:30)

The (t_{ion} and t_{ele}) number were calculated from the polarization current versus time plots using the equation's $t_{ion} = i_t - i_{ele} / i_t$ and $t_{ele} = i_{ele} / i_t$

Where i_t = initial current

And i_{ele} = residual current

The data which is given in table 1 indicates for all ratios of PVA+CH₃COONa 3H₂O polymer electrolyte systems the ionic transport number values are in between 0.96-0.98 which reveals that in polymer electrolyte films the charge

transport takes place mostly due to ions, and the electronic current is negligible. Mobility of ionic current in solid polymer films is measured by using transient ionic current method (5). The mobility of ions can be calculated using the equation

$$U = d^2 / TV$$

Where V = applied voltage (2.5V),

T = time of flight

D = thickness of sample.

The calculated mobility was found to be $2.37 \times 10^{-8} \text{ m}^2/\text{Vs}$ at (60:40) for PVA+CH₃COONa.3H₂O.

CONCLUSIONS

On proper mixture of pure PVA with CH₃COONa.3H₂O at different ratios to form solid polymer film. This is prepared by using solution casting technique. The system of PVA doped with 40%wt of sodium acetate trihydrate was exhibited the highest conductivity at $5.57 \times 10^{-6} \text{ S/cm}$ at room temperature 373K. The Arrhenius-type thermally activated process explains the temperature dependent of ionic conductivity in solid polymer electrolytes. From Hebb Wagner's Polarization technique, Ionic transport in solid polymer films are found to be at 0.96-0.98, which relates that the charge transport in these polymer electrolyte films are mostly due to Na⁺ ions.

ACKNOWLEDGEMENTS

The author thanks Er. K. Satyanarayana, President, Dr G.L. Datta (chancellor) and Dr. R. Sreehari Rao (Vice chancellor) of K L University for their constant encouragement. The authors also thank Dr A. Anand kumar their help and encouragement for providing laboratory facilities, kind supports and courage given for this work to be successfully completed. The authors also thank Faculty members of Department of physics K L University, for their cooperation.

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